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*by letter*



## BEHAVIOR OF BERYLLIUM SULFATE IN HARD AND SOFT WATER

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13. ABSTRACT The interaction of beryllium with hard and soft water represents the first phase of a study of beryllium effects on water and fish. The pH of BeSO <sub>4</sub> in soft water is significantly lower than in hard water over the concentration range from 0.01 to 100 mg/l Be(2+). An insoluble complex forms only in hard water within a limited beryllium concentration range. Water hardness <u>per se</u> is a significant determinant of the pH of beryllium solutions. The amount of NaHCO <sub>3</sub> needed to buffer varying amounts of concentrated (acidic) beryllium solutions is compared on a molar basis between soft and hard water. Beryllium has no effect on the hardness or dissolved oxygen content of either test water, but shows greater changes in conductivity of soft water than hard water. The absence of any appreciable beryllium effect on seven characteristics of soft or hard water over a 96-hour period supports the feasibility of running a static bioassay on beryllium in the laboratory.			

## SUMMARY

The pH of  $\text{BeSO}_4$  in soft water is significantly lower than in hard water at any given level over the concentration range from 0.01 to 200 mg/l  $\text{Be}^{2+}$ . In hard water only, a white, flocculent precipitate forms over a very small concentration range ( $> 1$  to  $< 50$  mg/l  $\text{Be}^{2+}$ ) with a pH from 5 to 7. Formation of this insoluble complex, which contains beryllium, hydroxide and carbonate ions, may depend in part on the amount and types of ions present in the aqueous medium. Several experiments showed water hardness per se to be a significant determinant of the pH of beryllium solutions.

Adding  $\text{NaHCO}_3$  to concentrated or acidic beryllium solutions in an amount either one-half or equal to the molar concentration of the beryllium salt raises the pH to levels adequate for fish bioassay work. Too much buffer, i.e., at or above two moles per mole of Be salt, causes precipitation. As expected, beryllium in soft water requires more buffering to achieve the same pH levels than it does in hard water. Adding small amounts of buffer to soft water (without the metal salt), which is slightly acidic, raises the pH to match that of hard water. The amount of  $\text{NaHCO}_3$  needed to buffer varying amounts of beryllium in solution is compared on a molar basis; differences in buffer action between soft and hard water are discussed.

The effects of beryllium on other characteristics of water were evaluated. It has no effect on the hardness and dissolved oxygen content of either hard or soft water. There are, however, relatively larger changes in the specific conductance of soft water than of hard water, reflecting a predominance of beryllium salt ions in water of low ionic strength. Under laboratory conditions, evaluation of a few beryllium solutions in bioassay test jars over a 96-hour period showed no appreciable change in pH, hardness, dissolved oxygen (DO), conductivity, temperature, fluid volume and physical appearance. These results support the feasibility of running a static bioassay on beryllium in the laboratory.

## FOREWORD

This study was conducted at the Toxic Hazards Division of the Aerospace Medical Research Laboratory, Wright-Patterson Air Force Base, Ohio. It was accomplished under Project 6302, "Toxic Hazards of Propellants and Materials," Task 630204, "Environmental Pollution Aspects of Propellants and Materials." This report covers the research conducted mostly during 1970 by the investigator, Dr. Arnold R. Slonim.

The author thanks the following individuals for various specialized analyses in support of this study: Messrs. J. Muntz and L. Roush, Air Force Materials Laboratory and Captain F. C. Damm, Air Force Institute of Technology, all at WPAFB - atomic absorption and emission spectroscopy; Major E. L. Arnold, Aerospace Medical Research Laboratory, WPAFB - gas chromatography; Mr. M. G. Schneider (SysteMed Corp., Dayton) - electrochemical analysis; and Messrs. J. V. Pustinger and W. D. Ross (Monsanto Research Corp., Dayton) - infrared and X-ray diffraction. In addition, the assistance of many personnel of SysteMed Corporation in collecting hard water samples and performing various other tasks is gratefully acknowledged. Special thanks are due Airman Edwin E. Ray, Aerospace Medical Research Laboratory for technical assistance with some of the work effort and Quentin H. Pickering of the Newtown (Ohio) Fish Toxicology Laboratory (Environmental Protection Agency) for many valuable discussions concerning bioassay studies, including the selection of some of the materials and analyses used for this phase of the program.

This technical report has been reviewed and is approved.

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## SECTION I

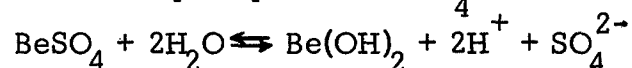
### INTRODUCTION AND BACKGROUND

Until recent times, various toxic materials, although handled with care relative to personal safety, have had no regulatory controls regarding their concentration in the environment. Because of the accumulation of certain toxic compounds on land, in water and air fatal to both man and livestock, the public has demanded efforts to curb pollution of the environment. Thus present efforts are being directed to determine the pollution potential of various toxic materials in use by the military and industry. One such material used extensively by both is beryllium (e.g., ref 1, 2). This study is concerned with determining the pollution potential of beryllium in water. For this purpose, beryllium sulfate, a soluble salt of the metal, is evaluated.

Although the major component of rocket motor exhaust products is beryllium oxide ( $\text{BeO}$ ), a highly toxic, relatively insoluble compound, a small amount of a water-soluble beryllium component exists also; this varies in concentration up to 12 mg/gram or 12,000 ppm (w/w) (ref 2, 3). Like some forms of  $\text{BeO}$ , water-soluble beryllium salts, such as  $\text{BeSO}_4$ , are very toxic. Similarly, inhalation of  $\text{BeSO}_4$  dust has been fatal to a variety of mammals (ref 4). Very scanty data, however, exist in the literature regarding the toxicity of beryllium salts to fish. In 1953, Pomelee (ref 5) reported on a small study in which  $\text{BeSO}_4$  was complexed with tartrate and added daily in small amounts to two aquariums each containing only two goldfish, 8 minnows, 3 snails and a few plants. Many problems (biological and mechanical) were cited in his methodology, and his experiment failed to demonstrate any beryllium toxicity so that the significance of his results, especially in the light of present-day standard bioassay methods, are subject to question. Tarzwell and Henderson in 1956 (ref 6) reported on the toxicity of the fathead minnow and bluegill to a variety of metals, including the sulfate, nitrate and chloride of beryllium. Unfortunately, no experimental details, including numbers of exposed fish were presented. Their tabulated data, however, showed approximately a 10- to 130-fold greater toxicity of the beryllium salts in soft water (20 mg/l) than in hard water (400 mg/l). Such results merit further study even if their statistical validity is unknown and so are considered here.

In general, differences in toxicity of substances between hard, natural water and soft water have been observed for many years (e.g., ref 7). The toxicity of various salts and metals for aquatic organisms are lower or less pronounced in hard water than in either soft or distilled water (for more details, see reviews by Doudoroff and Katz, ref 8, 9). This phenomenon is due probably to the buffering capacity of hard water, especially if it has a high carbonate/bicarbonate content, and also to calcium, which is known to antagonize such common cations as Na, K and Mg as well as certain very toxic metals to fish such as Pb, Zn and Cu (ref 9).

In spite of a number of chemical studies on beryllium solutions reported over a period of many years, such as the pH of  $\text{BeSO}_4$  at various concentrations and temperatures by Prytz in 1928 (ref 10), the electrochemical potential and behavior of the metal by Getman in 1934 (ref 11), and the hydrolysis of Be along with determination of some of the hydrolyzed products by Kakihamä and Sillen in 1956 (ref 12), the activity of Be in water is still not fully understood. This may partly be due to the complex nature of the metal, itself, and of its many chemical species, especially the different species formed in solution with oxygen and hydroxide (see, for example, ref 12). In a recent review of beryllium chemistry, Krejci and Scheel (ref 13) reported on a number of observations that were confirmed at several different laboratories; namely, beryllium acts as a cation in water below pH 5, "tends to form insoluble hydroxides or hydrated complex ions at pH 5 to 8, and will form beryllate-like complexes above pH 8." Moreover, strong acid salts of Be (e.g.,  $\text{BeSO}_4$  and  $\text{BeCl}_2$ ) hydrolyze to the same extent and to the same pH value for any given concentration. In addition to hydrolysis reactions, the conductivity of aqueous solutions of various Be salts was reviewed by the foregoing authors. Specific conductance data showed the hydrolysis of  $\text{BeSO}_4$



to be limited by the presence of hydrogen ions in the solution. "The relationships between the hydrogen ion, the beryllium ion, and the water molecules are essential to an understanding of the nature of the biologic interactions that can take place with beryllium in body tissues...Be salts will hydrolyze at the body pH to form first the basic salt ion or complex and then the insoluble  $\text{Be}(\text{OH})_2$ ." Since Be acts as a weak base, it tends to complex with weak acids, forming only very weakly ionized salts; this may account for the fixation of the metal by soft tissues as well as its poor elimination from the body (ref 13).

This report covers the first phase of the study of beryllium effects on water and fish. This phase is concerned mainly with the interaction of beryllium with hard and soft water. The work reported here will form the groundwork for subsequent phases of the program, such as the toxicity of  $\text{BeSO}_4$  in water, beryllium uptake by fish, response to beryllium under various conditions, the relationship between toxicity and water hardness, and the activity of the aforementioned relatively insoluble salt, beryllium oxide.

## SECTION II

### EXPERIMENTAL

#### ANALYTICAL METHODS

Water samples were analyzed in accordance with the procedures described in Standard Methods (ref 14) and in certain cases by specialized tests. Routine analyses of the water consisted of determining the pH, hardness (EDTA), specific conductance and dissolved oxygen. Dissolved oxygen was determined by instrumentation after calibration with the azide-Winkler wet chemical method. Tests for alkalinity and chlorine were conducted only in the beginning for selection of the source of raw hard water. In addition, some water samples were analyzed by other workers for calcium, magnesium, copper and iron by atomic absorption spectroscopy; a few samples to which  $\text{BeSO}_4$  was added were analyzed for beryllium content by a recent gas chromatographic technique (ref 15), and the nature of a beryllium precipitate in hard water was analyzed by infrared absorption, X-ray diffraction and emission spectroscopy.

#### MATERIALS<sup>1</sup>

The following instruments were used routinely in this study: Corning pH Meter, model 12; Conductivity Bridge, model RC 16B2 (Industrial Instruments, Inc., Cedar Grove, N. J.); YSI Oxygen Meter, model 54RC (Yellow Springs Instrument Co., Yellow Springs, Ohio); Corning Water Distillation Apparatus, model AG-2; and Mettler Digital Balance, model H6T. All chemical reagents used conformed to ACS specifications. The beryllium sulfate was in the form of  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ , which was obtained from Alfa Inorganics, Inc. (Beverly, Mass.). The glassware used for containing the beryllium solutions and later the fish for the bioassay studies consisted of wide-mouthed, 1-gallon size glass jars, purchased from the Cincinnati Container Co. (Cincinnati, Ohio). This glassware was found suitable for containing beryllium in the 100 to 0.01 mg/l range; no losses due to adsorption of Be onto glass were evident by isotope labelling (ref 16).

#### DISTILLED WATER

Commercially prepared distilled water was redistilled through an all-glass distillation apparatus (Corning). The distillate, which was collected and stored in a large (13 gal.) plastic carboy, had the following characteristics: pH of 6.3-6.4; specific conductance of 2 micromho/cm and no detectable calcium, magnesium and copper, that is, not above the limit of measurement of the atomic absorption instrument. The calcium content as measured with a

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<sup>1</sup>Names of companies do not constitute endorsement of the product by the U.S. Government, but are presented for information purposes only.

special Ca electrode was found to be less than 7 micromole/liter (or less than  $0.28 \mu\text{g/ml}$ ). This high quality water was used to make up all standard solutions, buffers and other reagents as well as serve as the diluent to make soft water from hard water and various bioassay test solutions.

#### RAW WATER SAMPLE

The source of raw hard water was ground water pumped from a well through stainless steel pipes into a small building adjacent to the laboratory. The lines were flushed for a minimum of 5 minutes before collecting the sample. A number of 9-liter narrow-mouthed collecting jars were used to collect the raw water via a rubber tube connection to the tap. The raw water, tinted brownish of varying degree from time to time depending upon the amount of iron present, was transported to the laboratory and left to stand for one week to allow sedimentation. Following this, the clear supernate was siphoned through a polyethylene tube into 8-inch diameter open jars (same as above 9-liter flasks but with top portions removed for easy cleaning after use) and then covered with a plexiglass sheet prior to use for making up test waters or water for different aquaria. This water contained no detectable chlorine, copper ( $< 0.01 \mu\text{g/ml}$ ) and iron ( $< 0.05 \mu\text{g/ml}$ ). It had a pH of 7.8 - 8.2, specific conductance of 700-870  $\mu\text{mho/cm}$ , hardness (EDTA) of 400-500 mg/l as  $\text{CaCO}_3$ , and dissolved oxygen (DO) of 6.8-7.65 mg/l.

#### HARD AND SOFT TEST WATERS

The raw water supernate, described above, was stored without further treatment and served as the "hard water" ( $\geq 400 \text{ mg/l as } \text{CaCO}_3$ ) for all tests. A 1:20 dilution of this supernate was made with glass distilled water and stored in an equal number of jars as for hard water; this was the "soft water" (20-25 mg/l as  $\text{CaCO}_3$ ). These respective test waters were used to make solutions of  $\text{BeSO}_4$  for the chemical studies described in this paper as well as serve as the media for the subsequent biological studies with fish (with and without beryllium).

#### BERYLLIUM SOLUTIONS

$\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$  was weighed within 0.1 mg and diluted to volume with either hard or soft water. The term  $\text{BeSO}_4$  or beryllium solution as used in this report refers to the aqueous solution of beryllium sulfate tetrahydrate. The beryllium solutions were tested in the concentration range from  $10^{-2}$  to  $10^2$  mg/l  $\text{Be}^{2+}$ . Throughout this study, beryllium concentrations are expressed in terms of the metal ion, except in instances where the molarity of the salt is noted.

### SECTION III

## RESULTS AND DISCUSSION

### EFFECTS ON pH

The pH values of  $\text{BeSO}_4$  in hard and soft water are presented in table I.<sup>2</sup> The values are the means of at least several determinations, with the range given in parenthesis (the range being omitted where only one or two determinations were made). The pH is significantly lower in soft water than in hard water for any given level of beryllium over the concentration range from 0.01 to 200 mg/l  $\text{Be}^{2+}$ . Beryllium at the lowest level tested (0.01 mg/l) is the same (pH) as the water without the metal. Starting at the 1.0 mg/l  $\text{Be}^{2+}$  level in either the hard or soft water series, the pH is reduced slightly and then continues to fall significantly as the beryllium content is increased. The pH curves for  $\text{BeSO}_4$  solutions are shown in figure 1. The largest difference between the curves (1.8 pH units) occurs at the 1.0 mg/l level, beyond which pH differences between hard and soft water become less with increasing Be concentrations (e.g., 0.7 at 100 mg/l and 0.4 at 200 mg/l  $\text{Be}^{2+}$ ). Extrapolation of both lines shows the intersection point to be at a pH of 2.3, which is approximately at the 1500 mg/l  $\text{Be}^{2+}$  level.

It has been observed that only in hard water over a very small beryllium concentration range - over 1.0 and less than 50 mg/l  $\text{Be}^{2+}$  - the water becomes cloudy and, on standing, a white flocculent precipitate forms. This phenomenon can occur by making beryllium solutions in hard water either by direct weighing or by diluting a concentrated, clear solution (e.g., 100 mg/l Be) down to a level within this range (e.g., 25 mg/l Be). Conversely, the turbidity can be cleared and the precipitate solubilized by mixing with a concentrated (acidic) Be solution, such as 100 or 200 mg/l Be. The fact that precipitation does not occur in (i) water of low ionic strength (soft water), (ii) hard water of very low levels of Be or alkaline pH, and (iii) hard water with Be levels  $\geq 50$  mg/l where the pH is below 5.0 suggests that hard water in the pH range 5 to 7 is suitable for forming insoluble beryllium complexes. An upper limit of pH 8 for forming insoluble complexes in water or a pH range of 5 to 8 for all water in general as suggested by Krejci and Scheel (ref 13) is not supported by these data; the discrepancy may be due to differences in the ionic strength and/or kinds of ions present in the water tested. The complex that forms in hard water in the Be concentration range cited was analyzed by infrared spectrometry (see appendix I) and X-ray diffraction and found to be noncrystalline in nature and a mixture of  $\text{BeCO}_3$  and  $\text{Be}(\text{OH})_2$  (ref 17).

TABLE I  
pH OF BERYLLIUM SULFATE IN HARD AND SOFT WATER

<u>Be<sup>2+</sup>, mg/l</u>	<u>HARD WATER *</u>	<u>SOFT WATER *</u>
0	7.90 (7.70 - 8.40)	6.42 (6.30 - 6.50)
0.01	7.90 (7.70 - 8.20)	6.40 (6.30 - 6.50)
0.1	7.60	6.25 (6.10 - 6.50)
1	7.35 (7.20 - 7.50)	5.55 (5.45 - 6.04)
5	6.40 +	- -
10	5.82 (5.30 - 6.20) +	4.41 (4.10 - 4.60)
50	4.80 (4.60 - 4.95)	- -
100	4.15 (4.05 - 4.25)	3.45 (3.40 - 3.70)
200	3.71 (3.65 - 3.73)	3.28 (3.20 - 3.30)

\* Hardness of hard water is  $\geq 400$  mg/l (as CaCO<sub>3</sub>) and soft water is 20 - 25 mg/l throughout study.

+ Turbid solution.

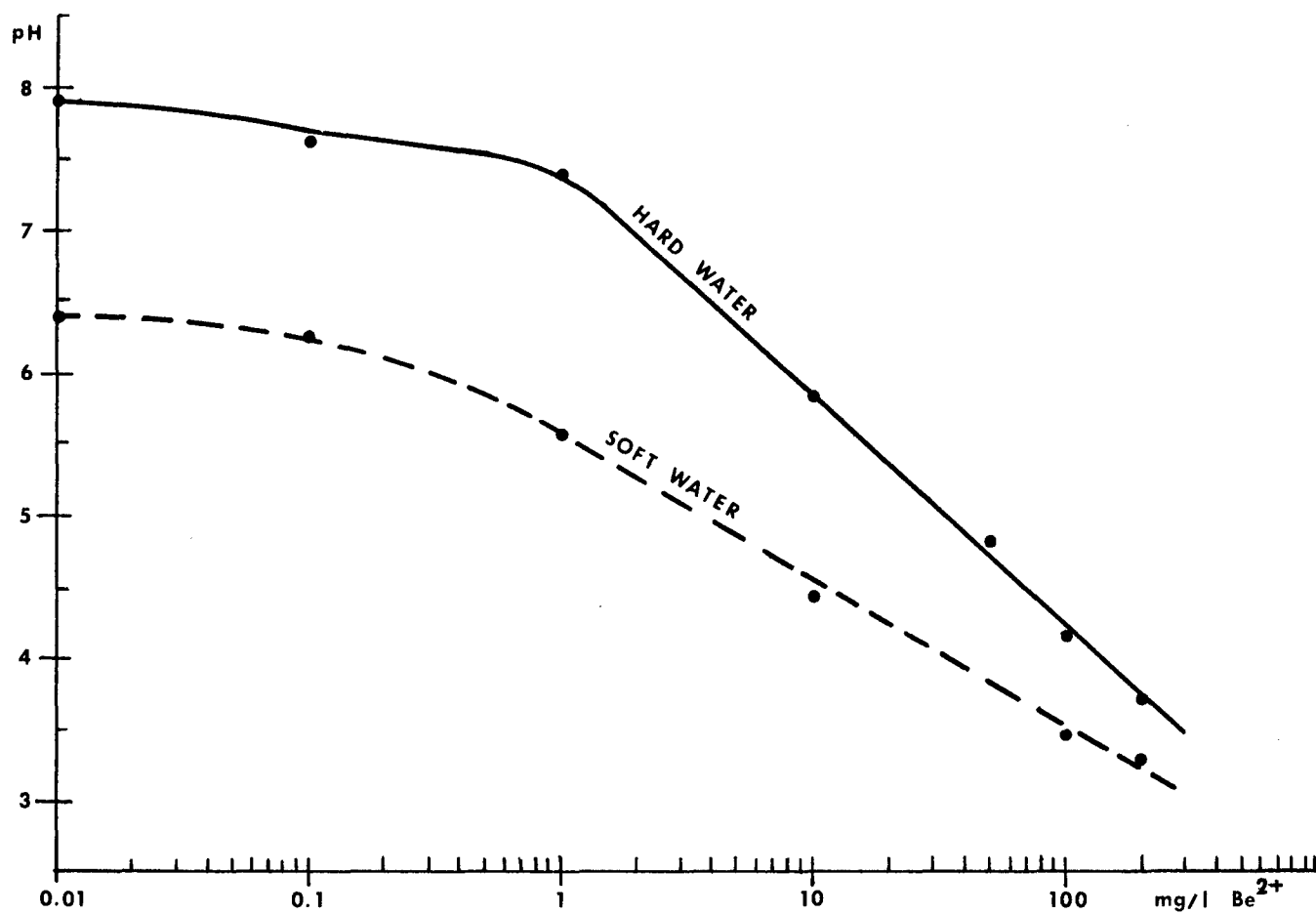


Figure 1: pH of beryllium sulfate in hard and soft water.

Since the pH of beryllium solutions is different between hard and soft water, the question arose as to what extent does water hardness influence the pH of such solutions. The foregoing results showed how the pH decreased with increasing amounts of beryllium when the hardness of the water was kept constant. The opposite conditions were next examined, that is, the effect on pH when the amount of beryllium was kept constant but water hardness was altered greatly. Table II shows the pH of 100 mg/l  $\text{Be}^{2+}$  (11.1 mM  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ ) in water varying in hardness from 451 to 21 mg/l. As expected, the pH is reduced as water hardness is decreased, although the pH change is relatively small. In another set of experiments, both the amount of beryllium and hardness of water of the same solution were serially diluted with distilled water, starting with 100 mg/l  $\text{Be}^{2+}$  in hard water, as shown in table III. The specific conductance reflects the relative concentration of ions present. The data show that pH remains relatively constant throughout the series, especially down to the level of 10 mg/l  $\text{Be}^{2+}$  and 50 mg/l hardness; thus, hardness tends to offset the effect of beryllium on pH. That a decrease in water hardness alone lowers the pH of beryllium solutions and that it offsets the effect of a proportional decrease in beryllium concentration indicate that water hardness per se is a significant determinant of the pH of beryllium solutions.

#### EFFECTS OF BUFFER

Since beryllium solutions become very acidic at high concentrations, buffering may be necessary as a countermeasure, especially when testing organisms at such levels in a bioassay. To maintain most species of tropical fish, a pH of 5 is minimally suitable (ref 8). In the following experiments, sodium bicarbonate ( $\text{NaHCO}_3$ , USP) was added to those beryllium test solutions having a low pH (see table I). This group of experiments was conducted to evaluate the effects of buffering the beryllium solutions, with an aim towards determining its applicability to later fish exposure studies.

The effect of increasing amounts of buffer on a constant amount of a concentrated or acidic solution of beryllium, 100 mg/l  $\text{Be}^{2+}$ , is shown in table IV. The pH of the  $\text{BeSO}_4$  solution is raised to at least 5.0 by adding 5.55 mM  $\text{NaHCO}_3$  in hard water, but double the amount (11.1 mM) in soft water. Addition of the equimolar concentration of  $\text{NaHCO}_3$  (11.1 mM) to beryllium in hard water, but not soft water, produces a turbid solution on standing, but this response is not consistent. Starting at 22.2 mM  $\text{NaHCO}_3$ , a flocculent precipitate is formed in either hard or soft water containing 11.1 mM  $\text{BeSO}_4$ , with more precipitation occurring as the amount of buffer is increased (For more turbidity data on buffered beryllium solutions, see appendix II). The tabulated data show further that a mixture of five moles of buffer to one mole of beryllium salt, although highly turbid, results in the same pH value (6.6) for soft and hard water. Since low concentrations of  $\text{NaHCO}_3$  form relatively clear mixtures with beryllium,

TABLE II  
pH of 11.1 mM  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$  (100 mg/l  $\text{Be}^{2+}$ ) IN  
WATER OF VARYING HARDNESS

<u>HARDNESS*</u> <u>(mg/l)</u>	<u>pH</u>
451	4.18
332	3.90
166	3.79
83	3.66
21	3.53

\* All tabulated carbonate hardness numbers are mean values determined by analysis.

TABLE III  
EFFECT OF VARYING PROPORTIONALLY THE AMOUNT  
OF BOTH BERYLLIUM AND WATER HARDNESS

<u>Be<sup>2+</sup></u> <u>(mg/l)</u>	<u>HARD.</u> <u>(mg/l)</u>	<u>pH</u>	<u>COND. *</u> <u>(μmho/cm)</u>
100 (undil)	424	4.2	1,560
50	212	4.2	900
25	108	4.3	520
10	48	4.6	265
1	4	5.3	86

\* A specific conductance of 1000 μmho/cm is equivalent to that of a 7.9 mM (590 mg/l) KCl standard solution (from calibration of instrument).

TABLE IV  
 BUFFERING OF 11.1 mM  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$  ( 100 mg/l Be) IN  
 HARD AND SOFT WATER: pH

<u><math>\text{NaHCO}_3</math> (mM)</u>	<u><math>\text{BeSO}_4/\text{NaHCO}_3</math> molar ratio</u>	pH	
		<u>HARD WATER</u>	<u>SOFT WATER</u>
0		4.15	3.42
5.55	2:1	4.98	4.24
11.1	1:1	5.47 (sl. turbid)	5.02
22.2	1:2	5.91 (turbid)	5.67 (turbid)
55.5	1:5	6.60 (turbid)	6.58 (turbid)
111	1:10	--	7.01 (turbid)

the effect of adding up to 11.1 mM  $\text{NaHCO}_3$  to water without beryllium was next examined. The data are presented in Table V; the relative concentration of ions present in solution is shown by the specific conductance values. There is no appreciable change in pH of hard water due to the bicarbonate buffer. A change to a slightly alkaline pH is evident on adding only 1.11 mM  $\text{NaHCO}_3$  to the soft water; whereas a pH of 8 (the same as for hard water) was attained by either 5.55 or 11.1 mM  $\text{NaHCO}_3$ .

The effect on pH of buffering different amounts of beryllium in hard and soft water was then evaluated. Table VI presents the results of several experiments in which the amount of  $\text{NaHCO}_3$  (0.055 - 22.2 mM) added to varying amounts of beryllium salt (0.111 - 11.1 mM) is compared on a molar basis. In hard water, no difference in pH exists upon adding 0.5 versus 1.0 mole of buffer per mole of beryllium salt at the 1 and 10 mg/l  $\text{Be}^{2+}$  levels; at the 100 mg/l  $\text{Be}^{2+}$  level, however, the more  $\text{NaHCO}_3$  added, the higher is the pH. In soft water, the same pH value exists for 0.5 mole as for 1.0 mole  $\text{NaHCO}_3$  per mole  $\text{BeSO}_4$  at the 1 mg/l  $\text{Be}^{2+}$  level; however, at the 10 and 100 mg/l levels, the pH is higher with the larger amount of bicarbonate added to the beryllium solution. Noted also is that the pH values at the 100 mg/l Be level in hard water are the same per molar ratio as those for 10 mg/l Be in soft water. As plotted in figure 2, these data show that in hard water equimolar amounts of buffer or half as much provide the same amount of buffer action, except at the 100 mg/l Be level; whereas in soft water the difference in buffer action increases gradually with increasing concentration of beryllium in solution. Moreover, at the 11.1 mM  $\text{BeSO}_4$  (100 mg/l  $\text{Be}^{2+}$ ) level, the same pH or buffer action is attained by 5.55 mM  $\text{NaHCO}_3$  in hard water as 11.1 mM buffer in soft water. Note, however, that this 2 to 1 relationship in soft and hard water, respectively, producing identical buffer action at the 100 mg/l Be level only, does not apply to higher beryllium concentrations as extrapolation of these curves indicates.

#### OTHER EFFECTS

The effects of increasing concentrations of beryllium on other characteristics of water were investigated, particularly those qualities that are relevant to fish bioassay studies (ref 14, 18). The following tests were run to determine if beryllium affects the hardness of the water, itself, and the dissolved oxygen content as well as alters quantitatively the specific conductance of hard and soft water. Table VII shows that beryllium does not alter the hardness of water or its dissolved oxygen content; the latter finding is important because it shows that any toxicity of beryllium to fish would be due not to oxygen depletion, but directly to the metal itself. The conductivity, on the other hand, is relatively unchanged up to 10 mg/l Be level in hard water, but is significantly higher at the 100 mg/l Be level, reflecting an increase in amount of electrolytes present; whereas in soft water, changes in specific conductance become appreciable

TABLE V  
EFFECT OF BUFFER ALONE ON HARD AND SOFT WATER

<u>NaHCO<sub>3</sub></u> <u>(mM)</u>	<u>HARD WATER</u>		<u>SOFT WATER</u>	
	<u>pH</u>	<u>COND.*</u>	<u>pH</u>	<u>COND.*</u>
0	8.05	750	6.50	52
1.11	7.90	835	7.40	148
5.55	8.00	1160	7.97	525
11.1	8.02	1535	8.08	915

\* See note under Table III

TABLE VI  
 BUFFERING OF VARYING AMOUNTS OF BERYLLIUM  
 SULFATE IN HARD AND SOFT WATER: pH

Be salt (mM)*	NaHCO <sub>3</sub> (mM) <sup>3</sup>	BeSO <sub>4</sub> /NaHCO <sub>3</sub> molar ratio <sup>3</sup>	pH	
			<u>HARD WATER</u>	<u>SOFT WATER</u>
0.111 (1)	0.055	2:1	7.65	6.10
	0.111	1:1	7.63	6.08
1.11 (10)	0.555	2:1	6.50 +	4.90
	1.11	1:1	6.57 +	5.45
11.1 (100)	5.55	2:1	4.98	4.24
	11.1	1:1	5.47 +	5.02
	22.2	1:2	5.91 ++	5.67

\* Values in parenthesis represent mg/l Be<sup>2+</sup> concentration. For pH of unbuffered beryllium at these levels, see Table I.

+ Slightly turbid      ++ Turbid

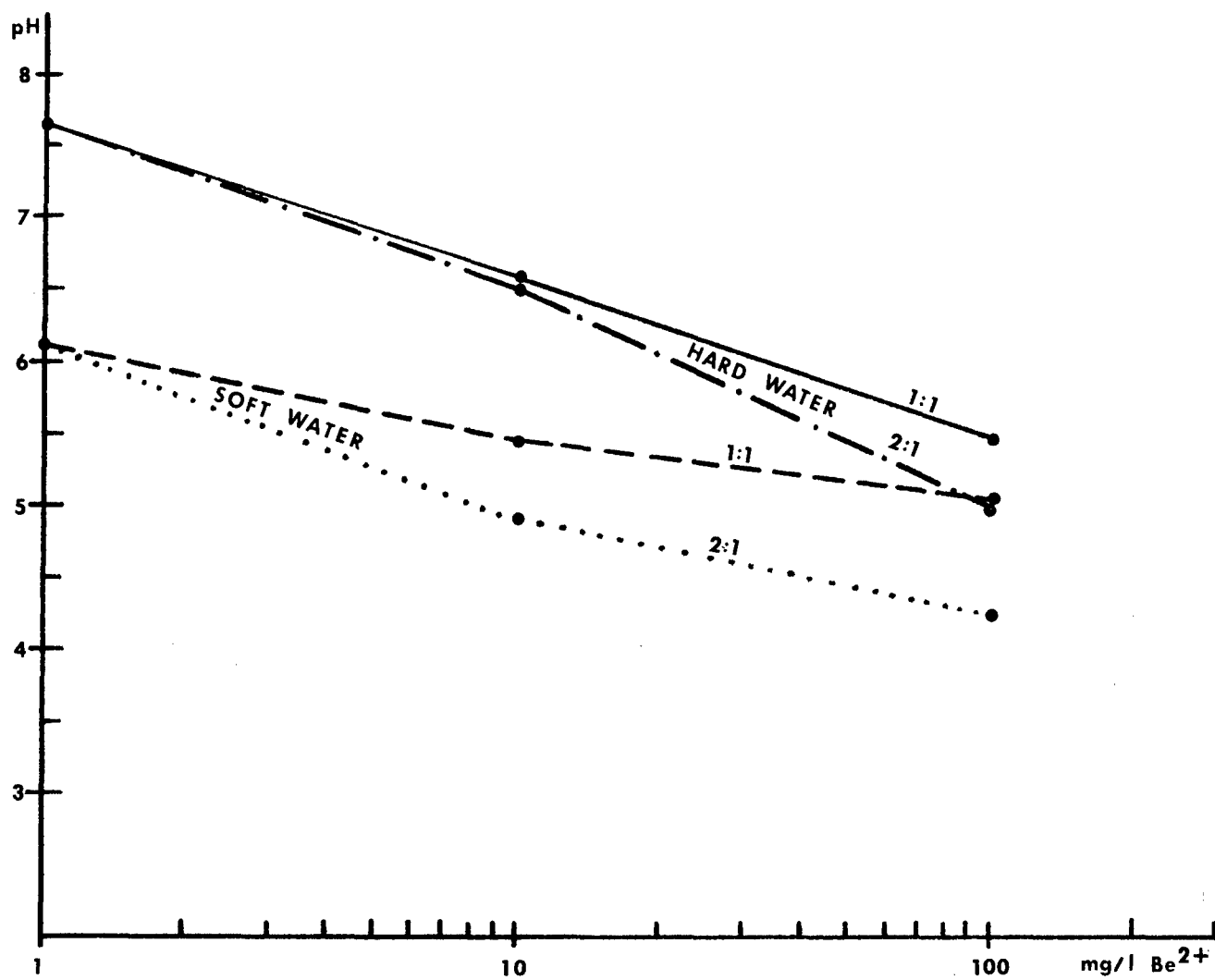


Figure 2: Buffering of beryllium sulfate in hard and soft water. Values on curves are molar ratios of Be salt to  $\text{NaHCO}_3$ .

TABLE VII  
BERYLLIUM EFFECTS ON HARDNESS, DISSOLVED OXYGEN,  
AND SPECIFIC CONDUCTANCE OF HARD AND SOFT WATER

Be <sup>2+</sup> (mg/l)	HARD WATER			SOFT WATER		
	HARD. (mg/l)	DO (mg/l)	COND. (μmho/cm)	HARD. (mg/l)	DO (mg/l)	COND. (μmho/cm)
0	392	7.75	720	24	7.75	62
0.01	396	7.70	727	24	7.65	58
1	405	7.70	770	24	7.65	84
10	400	7.78	790	24	7.70	282
100	405	7.78	1,740	26	7.70	1,490

at the 10 mg/l level and are significantly larger at the 100 mg/l Be level, reflecting a predominance of beryllium salt ions over the relatively few others that exist in soft water.

Since a bioassay by the standard method requires up to a 96-hour evaluation period (ref 14), a few representative solutions (control, 1.0 and 100 mg/l  $\text{Be}^{2+}$ ) were evaluated under laboratory conditions for changes in pH, hardness, dissolved oxygen and conductivity, and, to a less extent, in temperature, volume and physical appearance (e.g., turbidity) during this period. Table VIII shows that none of the characteristics measured previously is affected by beryllium over a 96-hour period. It is especially noteworthy that the amount of dissolved oxygen is not only unaltered for 96 hours but well above the recommended minimal DO threshold limit for testing fish (ref 14). During this period also, the temperature remained constant ( $23.9 \pm 0.5^\circ\text{C}$ ), fluid volume in the test jars was not changed noticeably with time, and all solutions were clear. These results, from both the tabulated and untabulated data, support the feasibility of running a static bioassay with beryllium in the laboratory in contrast to the more difficult and stringent continuous-flow procedure.

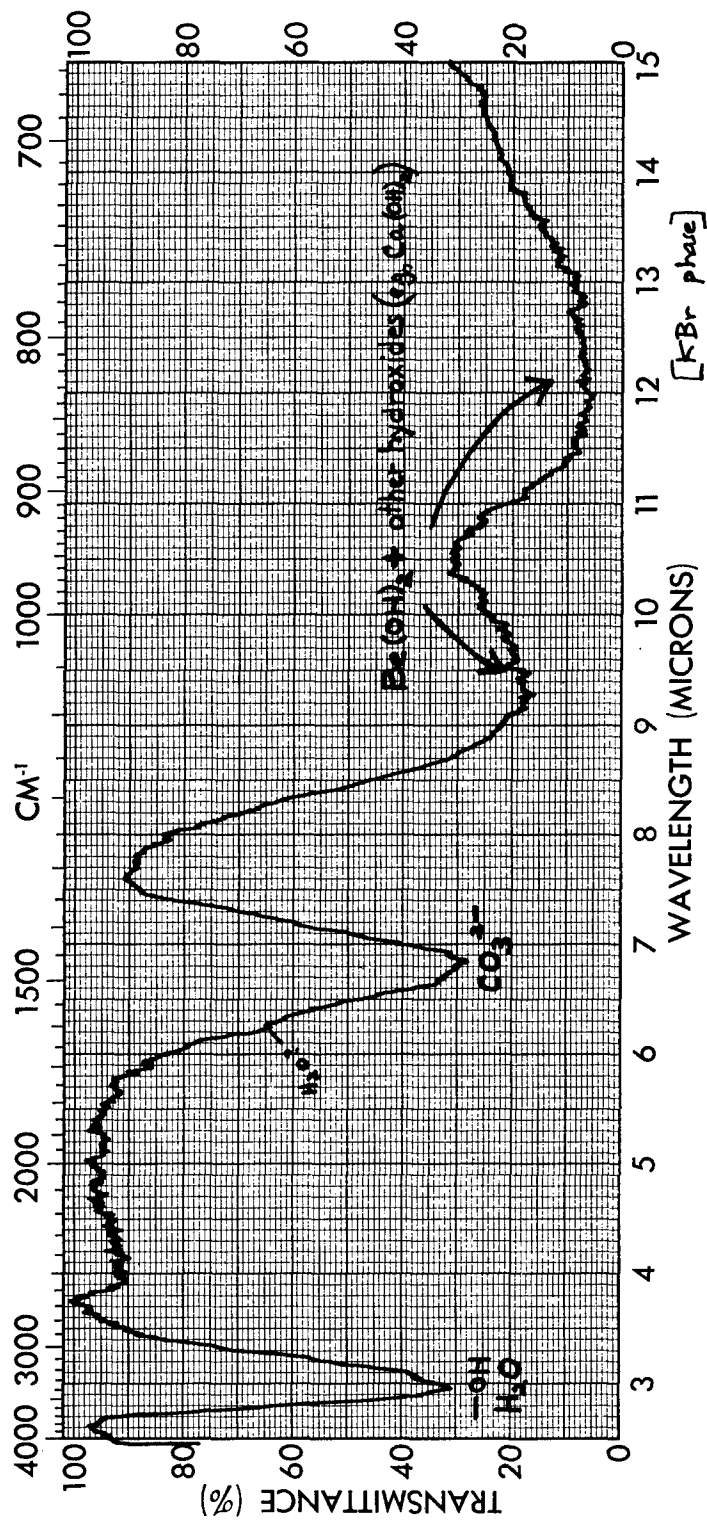
TABLE VIII  
BERYLLIUM EFFECTS IN HARD AND SOFT WATER  
DURING A 96-HOUR PERIOD

Be <sup>2+</sup> (mg/l)	pH		HARD.*		DO*		COND.*	
	0	96hr	0	96hr	0	96hr	0	96hr
HARD WATER								
0	7.95	7.90	392	400	7.75	7.75	720	720
1	7.30	7.40	408	400	7.70	7.80	723	775
100	4.15	4.20	408	412	7.78	7.75	1,740	1,780
SOFT WATER								
0	6.42	6.45	24	26	7.75	7.75	58	62
1	5.60	5.60	24	24	7.65	7.60	77	84
100	3.45	3.42	26	28	7.70	7.75	1,490	1,535

\* Same units as Table VII

# APPENDIX I

## INFRARED SPECTRUM OF BERYLLIUM PRECIPITATE IN HARD WATER



(Courtesy of Ross and Pustinger, ref 17)

APPENDIX II

EFFECT ON TURBIDITY OF BERYLLIUM AND BUFFER

MIXTURES IN WATER OF DIFFERENT HARDNESS

<u>BeSO<sub>4</sub>, mM</u>	<u>NaHCO<sub>3</sub>, mM</u>	<u>A:B</u>	<u>TURBIDITY</u>		
			<u>20</u>	<u>280</u>	<u>452 mg/l hardness</u>
11.1	5.55	2:1	-	-	-
11.1	11.1	1:1	-	-	-/+
11.1	22.2	1:2	+	+	+
11.1	55.5	1:5	++	++	++
11.1	111	1:10	++		

- 
- : negative (clear solution)
  - /+ : trace to slight turbidity on standing
  - + : turbid (flocculent precipitate)
  - ++ : very turbid (heavy precipitate)

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